

## ION-CONDUCTING POLYMERIC MATERIALS

### BACKGROUND

[0001] This invention relates to ion-conducting polymeric materials and particularly, although not exclusively, relates to a method of preparing a formulation of an ion-conducting polymeric material and such a formulation per se. Preferred embodiments relate to the use of formulations prepared in the manufacture of coatings or films of ion-conducting polymeric materials.

### BRIEF DESCRIPTION OF THE DRAWINGS

[0002] FIGURE 1 illustrates a cross-sectional view of a polymer electrolyte membrane fuel cell according to the one embodiment of the subject invention.

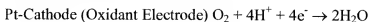
### DETAILED DESCRIPTION

[0003] One type of polymer electrolyte membrane fuel cell (PEMFC), shown schematically in Figure 1 of the accompanying diagrammatic drawings, may comprise a thin sheet 2 of a hydrogen-ion conducting Polymer Electrolyte Membrane (PEM) sandwiched on both sides by a layer 4 of platinum catalyst and an electrode 6. The layers 2, 4, 6 make up a Membrane Electrode Assembly (MEA) of less than 1mm thickness.

[0004] In a PEMFC, hydrogen is introduced at the anode (fuel electrode) which results in the following electrochemical reaction:



[0005] The hydrogen ions migrate through the conducting PEM to the cathode. Simultaneously, an oxidant is introduced at the cathode (oxidant electrode) where the following electrochemical reaction takes place:



[0006] Thus, electrons and protons are consumed to produce water and heat. Connecting the two electrodes through an external circuit causes an electrical current to flow in the circuit and withdraw electrical power from the cell.

[0007] Preferred ion-conducting polymeric materials for use as components of polymer electrolyte membranes in fuel cells have high conductivity (low EW, or high ion-exchange

capacities), optimum water uptake for good conductivity and mechanical properties and solubility in solvents which can be used to cast the membranes.

**[0008]** Examples of known ion-conducting polymeric materials are described in US 5985477 (Sumitomo) and US 5906716 (Hoechst). The polyaryletherketones and/or sulfones described are dissolved in a solvent, usually N-methylpyrrolidone (NMP), and are then cast to prepare membranes.

**[0009]** Whilst NMP is a very good solvent for casting membranes from a wide range of materials, membranes cast from NMP (especially polymer electrolyte membranes of fuel cells) can have defects and/or exhibit problems in downstream process steps. Furthermore, it is preferred for environmental and safety reasons to minimize the amounts of organic solvents used in chemical processes.

**[0010]** It is an object of the present invention to address problems associated with the preparation and/or use of formulations of ion-conducting polymeric materials.

**[0011]** According to a first aspect of the present invention, there is provided a method of preparing a formulation comprising an ion-conducting polymeric material, the method comprising: (a) selecting an ion-conducting polymeric material of a type which includes: (i) phenyl moieties; (ii) carbonyl and/or sulfone moieties; and (iii) ether and/or thioether moieties; (b) selecting a solvent mixture comprising water and a first organic solvent in which mixture the ion-conducting polymeric material can be dissolved and/or dispersed; (c) dissolving and/or dispersing the ion-conducting polymeric material in the solvent mixture; (d) removing greater than 80% of the total amount of the first organic solvent in the solvent mixture, thereby to leave a formulation comprising the ion-conducting polymeric material dissolved and/or dispersed in a solvent formulation comprising a major amount of water.

**[0012]** Surprisingly, it has been found that a stable solution and/or dispersion of the polymeric material in a substantial amount of water can be prepared in the method which solution/dispersion would not generally be preparable by simply attempting to dissolve/disperse the polymeric material in a solvent formulation comprising the same amount of water, without the use of steps (b) to (d) of the method.

**[0013]** The formulations prepared in the method appear to the naked eye to be solutions; however, they are probably not true solutions but more likely are very fine dispersions of the ion-conducting polymeric material in the solvent formulation.

**[0014]** The first organic solvent selected in step (b) is preferably water miscible at 25°C. The first organic solvent preferably has a boiling point of less than that of water. The boiling point of the first organic solvent may be less than 95°C, suitably less than 90°C, preferably less than 85°C, more preferably less than 80°C, especially less than 75°C, at atmospheric pressure. The boiling point may be greater than 30°C, suitably greater than 40°C, preferably greater than 50°C, more preferably greater than 55°C at atmospheric pressure.

**[0015]** The first organic solvent may have up to five, preferably up to four, carbon atoms. Preferably, the first organic solvent has two to four carbon atoms. The first organic solvent preferably includes a[[n]] hydroxy, ether or carbonyl functional group. Preferably, the first organic solvent includes only one of the functional groups. The first organic solvent preferably does not include any other functional groups. The first organic solvent preferably does not include any halogen atoms. The first organic solvent is preferably saturated. The solvent may be selected from alcohols, ethers (including cyclic ethers) and ketones, especially C<sub>2-4</sub> alcohols, ethers and ketones. Especially preferred first organic solvents are acetone, methylethylketone, ethanol and tetrahydrofuran.

**[0016]** The solvent mixture selected in step (b) may include more than one organic solvent and each may be as described in any statement herein.

**[0017]** In one embodiment, the solvent mixture may include an optional second organic solvent. The second organic solvent may have a boiling point which is greater than that of the first organic solvent so that the first organic solvent is preferentially removed in step (d) and, preferably, less than 10 wt%, more preferably less than 5 wt%, especially less than 1 wt%, of the second organic solvent is removed in step (d). The second organic solvent may have a boiling point at atmospheric pressure which is at least 20°C greater than the boiling point of the first organic solvent. The second organic solvent may be included to facilitate the preparation of articles, for example films, in accordance with the third aspect described hereinafter. The second organic solvent may act as a coalescing agent during film formation. However, it is preferred for the second organic solvent to be included (if included at all) after step (d). Examples of second solvents are N-methylpyrrolidene and glycols such as ethylene glycol.

**[0018]** The ratio of the wt% of water to the wt% of the first organic solvent (preferably to the wt% of the total amount of organic solvent(s) in the mixture) is suitably in the range 0.25 to 2.5, preferably in the range 0.4 to 2.3 and, more preferably, in the range 0.5 to 1.5.

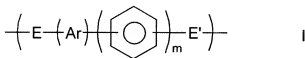
**[0019]** Suitably, the solvent mixture of step (c) includes at least 1 wt%, preferably at least 3 wt%, more preferably at least 7 wt%, especially at least 9 wt% of the ion-conducting polymeric material. The solvent mixture may include less than 20 wt%, preferably less than 15 wt%, especially less than 12 wt% of the ion-conducting polymeric material.

**[0020]** Step (c) of the method is preferably carried out at a temperature which is less than the boiling point of the solvent mixture. Thus, step (c) preferably comprises dissolving and/or dispersing the ion-conducting polymeric material in the solvent mixture under conditions at which the solvent mixture is not boiling. Suitably, step (c) is carried out at ambient temperature (eg 20°C) or above and at less than the boiling point of the solvent mixture.

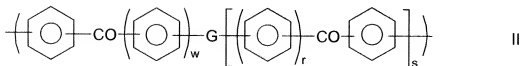
**[0021]** Step (d) suitably includes removing greater than 85%, preferably greater than 90%, more preferably greater than 95 wt%, especially greater than 99 wt% of the first organic solvent in step (d). Preferably, substantially the entirety of the first organic solvent is removed in step (d).

**[0022]** The first organic solvent is preferably evaporated off in step (d), suitably under a pressure of less than atmospheric pressure. After removal of the first organic solvent, the solvent formulation which includes a major amount of water suitably includes at least 10 wt%, preferably at least 14 wt%, more preferably at least 18 wt% of the ion-conducting polymeric material in the solvent formulation. The solvent formulation may include less than 30 wt% or less than 25 wt% of the ion-conducting polymeric material. However, a solvent formulation which is more concentrated in the ion-conducting polymeric material may be prepared by removing, for example evaporating, some of the water in the solvent formulation which includes a major amount of water. In this event, the solvent formulation which includes a major amount of water may include at least 30 wt%, at least 40 wt% or even 50 wt% of the ion-conducting polymeric material.

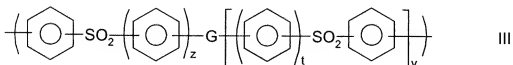
**[0023]** The ion-conducting polymeric material may include a moiety of formula



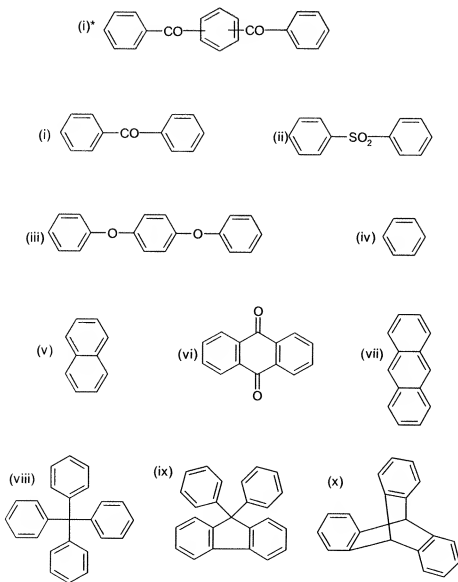
and/or a moiety of formula



and/or a moiety of formula



wherein at least some of the units I, II and/or III are functionalized to provide ion-exchange sites, wherein the phenyl moieties in units I, II, and III are independently optionally substituted and optionally cross-linked; and wherein m,r,s,t,v,w and z independently represent zero or a positive integer, E and E' independently represent an oxygen or a sulfur atom or a direct link, G represents an oxygen or sulfur atom, a direct link or a -O-Ph-O- moiety where Ph represents a phenyl group and Ar is selected from one of the following moieties (i)\* or (i) to (x) which is bonded via one or more of its phenyl moieties to adjacent moieties.



**[0024]** Unless otherwise stated in this specification, a phenyl moiety may have 1,4- or 1,3-, especially 1,4-, linkages to moieties to which it is bonded.

**[0025]** In (i)\*, the middle phenyl may be 1,4- or 1,3- substituted.

**[0026]** Suitably, to provide the ion exchange sites, the polymeric material is sulfonated, phosphorylated, carboxylated, quaternary-aminoalkylated or chloromethylated, and optionally further modified to yield  $-\text{CH}_2\text{PO}_3\text{H}_2$ ,  $-\text{CH}_2\text{NR}_3^{20+}$  where  $\text{R}^{20}$  is an alkyl, or  $-\text{CH}_2\text{NAr}_3^{x+}$  where  $\text{Ar}^x$  is an aromatic (arene), to provide a cation or anion exchange membrane. Further still, the aromatic moiety may contain a hydroxyl group which can be

readily elaborated by existing methods to generate  $-\text{OSO}_3\text{H}$  and  $-\text{OPO}_3\text{H}_2$  cationic exchange sites on the polymer. Ion exchange sites of the type stated may be provided as described in WO95/08581.

[0027] Preferably, the polymeric material is sulfonated. Preferably, the only ion-exchange sites of the polymeric material are sites which are sulfonated.

[0028] References to sulfonation include a reference to substitution with a group  $-\text{SO}_3\text{M}$  wherein M stands for one or more elements selected with due consideration to ionic valencies from the following group: H,  $\text{NR}_4^{y+}$ , in which  $\text{R}^y$  stands for H,  $\text{C}_1$ - $\text{C}_4$  alkyl, or an alkali or alkaline earth metal or a metal of sub-group 8, preferably H,  $\text{NR}_4^+$ , Na, K, Ca, Mg, Fe, and Pt. Preferably M represents H. Sulfonation of the type stated may be provided as described in WO96/29360.

[0029] The polymeric material may include more than one different type of repeat unit of formula I; more than one different type of repeat unit of formula II; and more than one different type of repeat unit of formula III.

[0030] The moieties I, II and III are suitably repeat units. In the polymeric material, units I, II and/or III are suitably bonded to one another - that is, with no other atoms or groups being bonded between units I, II, and III.

[0031] Where the phenyl moieties in units I, II or III are optionally substituted, they may be optionally substituted by one or more halogen, especially fluorine and chlorine, atoms or alkyl, cycloalkyl or phenyl groups. Preferred alkyl groups are  $\text{C}_{1-10}$ , especially  $\text{C}_{1-4}$ , alkyl groups. Preferred cycloalkyl groups include cyclohexyl and multicyclic groups, for example adamantyl. In some cases, the optional substituents may be used in the cross-linking of the polymer. For example, hydrocarbon optional substituents may be functionalized, for example sulfonated, to allow a cross-linking reaction to take place. Preferably, the phenyl moieties are unsubstituted.

[0032] Another group of optional substituents of the phenyl moieties in units I, II or III include alkyls, halogens,  $\text{C}_y\text{F}_{2y+1}$  where y is an integer greater than zero,  $\text{O}-\text{R}^q$  (where  $\text{R}^q$  is selected from the group consisting of alkyls, perfluoroalkyls and aryls),  $\text{CF}=\text{CF}_2$ , CN,  $\text{NO}_2$  and OH. Trifluoromethylated phenyl moieties may be preferred in some circumstances.

[0033] Where the polymeric material is cross-linked, it is suitably cross-linked so as to improve its properties as a polymer electrolyte membrane, for example to reduce its

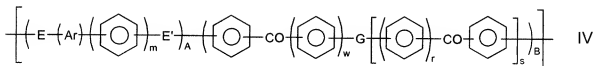
swellability in water. Any suitable means may be used to effect cross-linking. For example, where E represents a sulfur atom, cross-linking between polymer chains may be effected via sulfur atoms on respective chains. Alternatively, the polymer may be cross-linked via sulfonamide bridges as described in US 5 561 202. A further alternative is to effect cross-linking as described in EP-A-0008895.

**[0034]** Where w and/or z is/are greater than zero, the respective phenylene moieties may independently have 1,4- or 1,3-linkages to the other moieties in the repeat units of formulae II and/or III. Preferably, the phenylene moieties have 1,4- linkages.

**[0035]** Preferably, the polymeric chain of the first material does not include a -S- moiety. Preferably, G represents a direct link.

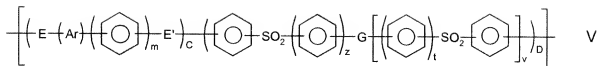
**[0036]** Suitably, "a" represents the mole % of units of formula I in the polymeric material, suitably wherein each unit I is the same; "b" represents the mole % of units of formula II in the material, suitably wherein each unit II is the same; and "c" represents the mole % of units of formula III in the material, suitably wherein each unit III is the same. Preferably, a is in the range 45-100, more preferably in the range 45-55, especially in the range 48-52. Preferably, the sum of b and c is in the range 0-55, more preferably in the range 45-55, especially in the range 48-52. Preferably, the ratio of a to the sum of b and c is in the range 0.9 to 1.1 and, more preferably, is about 1. Suitably, the sum of a, b and c is at least 90, preferably at least 95, more preferably at least 99, especially about 100. Preferably, the polymeric material consists essentially of moieties I, II and/or III.

**[0037]** The polymeric material may be a homopolymer having a repeat unit of general formula



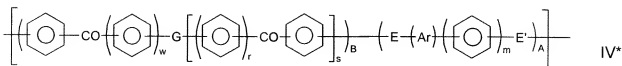
or a homopolymer having a repeat unit of general formula



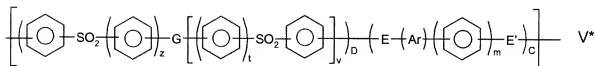


or a random or block copolymer of at least two different units of IV and/or V provided that repeat units (or parts of repeat unit) are functionalized to provide ion-exchange sites; wherein A, B, C and D independently represent 0 or 1 and E, E', G, Ar, m, r, s, t, v, w and z are as described in any statement herein.

**[0038]** As an alternative to a polymer comprising units IV and/or V discussed above, the polymeric material may be a homopolymer having a repeat unit of general formula

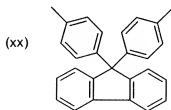
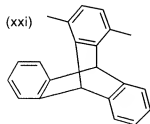
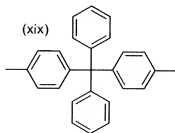
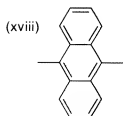
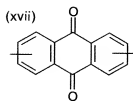
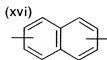
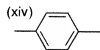
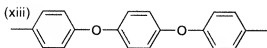
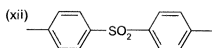
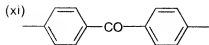
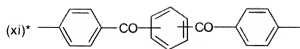


or a homopolymer having a repeat unit of general formula



or a random or block copolymer of at least two different units of IV\* and/or V\* provided that repeat units (or parts of repeat units) are functionalized to provide ion-exchange sites; wherein A, B, C, and D independently represent 0 or 1 and E, E', G, Ar, m, r, s, t, v, w and z are as described in any statement herein.

**[0039]** Preferably, m is in the range 0-3, more preferably 0-2, especially 0-1. Preferably, r is in the range 0-3, more preferably 0-2, especially 0-1. Preferably t is in the range 0-3, more preferably 0-2, especially 0-1. Preferably, s is 0 or 1. Preferably v is 0 or 1. Preferably, w is 0 or 1. Preferably z is 0 or 1.



**[0040]** Preferably Ar is selected from the following moieties (xi)\* and (xi) to (xxi): In (xi)\*, the middle phenyl may be 1,4- or 1,3- substituted.

[0041] Preferably, (xv) is selected from a 1,2-, 1,3-, or a 1,5- moiety; (xvi) is selected from a 1,6-, 2,3-, 2,6- or a 2,7- moiety; and (xvii) is selected from a 1,2-, 1,4-, 1,5-, 1,8- or a 2,6- moiety.

[0042] Unless otherwise stated in this specification, a reference to a crystalline material extends to any material having at least some crystallinity.

[0043] The existence and/or extent of crystallinity in a polymer is preferably measured by wide angle X-ray diffraction, for example as described by Blundell and Osborn (Polymer 24, 953, 1983). Alternatively, Differential Scanning Calorimetry (DSC) could be used to assess crystallinity. The level of crystallinity in the polymeric material may be 0% (e.g. where the material is amorphous or crystallisable); or the level of crystallinity may be at least 0.5%, suitably at least 1%, preferably at least 5% weight fraction, suitably when measured as described by Blundell and Osborn. The level of crystallinity in the polymeric material may be less than 20%.

[0044] Suitable moieties Ar are moieties (i)\*, (i), (ii), (iv) and (v) and, of these, moieties (i)\*, (i), (ii) and (iv) are preferred. Preferred moieties Ar are moieties (xi)\*, (xi), (xii), (xiv), (xv) and (xvi) and, of these, moieties (xi)\*, (xi), (xii) and (xiv) are especially preferred. Another preferred moiety is moiety (v), especially, moiety (xvi). In relation, in particular to the alternative first polymeric materials comprising units IV\* and/or V\*, preferred Ar moieties are (v) and, especially, (xvi).

[0045] One preferred class of polymeric materials may include at least some ketone moieties in the polymeric chain. In such a preferred class, the polymer preferably does not only include -O- and -SO<sub>2</sub>- moieties between aryl (or other unsaturated) moieties in the polymeric chain. Thus, in this case, suitably, a polymer of the first aspect does not consist only of moieties of formula III, but also includes moieties of formula I and/or II.

[0046] Preferred polymeric materials include -ether-biphenyl-ether-phenyl-ketone- units. Preferred polymeric materials may additionally include -ether-phenyl-sulfone-phenyl-ether-phenyl-ketone- units. Optionally, preferred polymeric materials may include -ether-phenyl-sulfone-phenyl-ether-phenyl-ketone- units.

[0047] Where a phenyl group is sulfonated, it may be mono-sulfonated.

[0048] The glass transition temperature ( $T_g$ ) of the ion-conducting polymeric material may be at least 144°C, suitably at least 150°C, preferably at least 154°C, more preferably at

least 160°C, especially at least 164°C. In some cases, the T<sub>g</sub> may be at least 170°C, or at least 190°C or greater than 250°C or even 300°C.

[0049] The polymeric material may have an inherent viscosity (IV) of at least 0.1, suitably at least 0.3, preferably at least 0.4, more preferably at least 0.6, especially at least 0.7 (which corresponds to a reduced viscosity (RV) of least 0.8) wherein RV is measured at 25°C on a solution of the polymer in concentrated sulfuric acid of density 1.84gcm<sup>-3</sup>, the solution containing 1g of polymer per 100cm<sup>-3</sup> of solution. IV is measured at 25°C on a solution of polymer in concentrated sulfuric acid of density 1.84gcm<sup>-3</sup>, the solution containing 0.1g of polymer per 100cm<sup>-3</sup> of solution. The measurements of both RV and IV both suitably employ a viscometer having a solvent flow time of approximately 2 minutes.

[0050] The equivalent weight (EW) of the ion-conductive polymeric material is preferably less than 850g/mol, more preferably less than 800g/mol, especially less than 750g/mol. The EW may be greater than 300, 400 or 500 g/mol.

[0051] The boiling water uptake of ion-conductive polymeric material measured as described hereinafter is suitably less than 350%, preferably less than 300%, more preferably less than 250%.

[0052] The main peak of the melting endotherm (T<sub>m</sub>) for the first polymeric material may be at least 300°C.

[0053] According to a second aspect of the invention, there is provided a polymeric material containing formulation (hereinafter "the pmc formulation") which comprises an ion-conducting polymeric material dissolved and/or dispersed in a solvent formulation wherein: (a) the ion-conducting polymeric material includes: (i) phenyl moieties; (ii) carbonyl and/or sulfone moieties; and (iii) ether and/or thioether moieties; and (b) greater than 50 wt% of the solvent formulation is made up of water.

[0054] Suitably, at least 55 wt%, preferably at least 60 wt%, of the solvent formulation is made up of water. In embodiments wherein a second organic solvent is included in [[said]] solvent mixture, the pmc formulation may include a second organic solvent as described above. The solvent formulation of the second aspect may include 0-40 wt% of the second solvent formulation. In preferred embodiments at least 95 wt%, especially at least 99 wt% of the solvent formulation of the second aspect is made up of water. In especially preferred embodiments, the solvent formulation consists essentially of water.

[0055] The pmc formulation may include at least 1 wt%, suitably at least 3 wt%, preferably at least 7 wt%, more preferably at least 9 wt% of the ion-conducting polymeric material (or if more than one type of polymeric material is included, the total amount of polymeric materials may be as aforesaid). In some situations, the pmc formulation may include greater than 30 wt%, or even greater than 40 wt% of the polymeric material(s).

[0056] The pmc formulation is preferably a stable solution/dispersion – that is, the polymeric material does not substantially precipitate over time.

[0057] According to a third aspect of the present invention, there is provided a method of fabricating an article, the method including the step of contacting a member with a formulation according to the first or second aspects. The method may be used to deposit the polymeric material on the member. For example, the member may be a support which may be contacted with the formulation in order to prepare a membrane; or the support may be coated with the formulation and/or the ion-conducting polymeric material in order to prepare an article which comprises the member and a coating prepared as described.

[0058] The method of the third aspect may be used in fabricating a wide range of types of articles. In one embodiment, the formulation may be used to impregnate the member, for example a fiber or fabric. In this event, the solvent mixture may not include a the second organic solvent as described above. In another embodiment, the formulation may be used to form a film in which case, the solvent mixture may include a the second organic solvent. In either case, the method may be advantageous since the solvent mixture includes a major amount of water, rather than a major amount of organic solvent and is consequently easier to handle. Furthermore, it is found that a formulation according to the first or second aspects may include a relatively high concentration of the polymeric material (eg greater than 50 wt%) and, therefore, removal of solvents from the formulation after contact with the member may require less energy.

[0059] Any feature of any aspect of any invention or embodiment described herein may be combined with any feature of any aspect of any other invention or embodiment described herein mutatis mutandis.

[0060] Specific embodiments of the invention will now be described, by way of example, with reference to figure 1 which is a schematic representation of a polymer electrolyte membrane fuel cell.

### Example 1a

[0061] A 700ml flanged flask fitted with a ground glass Quickfit lid, stirrer/stirrer guide, nitrogen inlet and outlet was charged with 4,4'-difluorobenzophenone ( 89.03g, 0.408 mole, mole ratio = 1.02), 4,4'-dihydroxybiphenyl (24.83g, 0.133 mole, mole ratio = 0.33), 4,4'-dihydroxydiphenylsulfone (53.65g, 0.213 mole, mole ratio = 0.536), 4,4'-dihydroxybenzophenone (11.37g, 0.053 mole, mole ratio = 0.134) and diphenylsulfone (332g) and purged with nitrogen for over 1 hour. The contents were then heated under a nitrogen blanket to between 140 and 150°C to form an almost colorless solution. While maintaining a nitrogen blanket, dried sodium carbonate (43.24g, 0.408 mole) was added. The temperature was raised gradually to 320°C over 3 hours then maintained for 1.5 hours.

[0062] The reaction mixture was allowed to cool, milled and washed with acetone and water. The resulting polymer was dried in an air oven at 120°C. The polymer had a melt viscosity at 400°C, 1000sec<sup>-1</sup> of 0.34 kNsm<sup>-2</sup>.

### Example 2a

[0063] A 700ml flanged flask fitted with a ground glass Quickfit lid, stirrer/stirrer guide, nitrogen inlet and outlet was charged with 4,4'-difluorobenzophenone (89.03g, 0.408 mole, mole ratio = 1.02), 4,4'-dihydroxybiphenyl, (24.93g, 0.133 mole, mole ratio = 0.33), 4,4'-dihydroxydiphenylsulfone (66.73g, 0.267 mole, mole ratio = 0.67) and diphenylsulfone (332g) and purged with nitrogen for over 1 hour. The contents were then heated under a nitrogen blanket to between 140 and 150°C to form an almost colorless solution. While maintaining a nitrogen blanket, dried sodium carbonate (42.44g, 0.40 mole) and potassium carbonate (1.11g, 0.008 mole) were added. The temperature was raised gradually to 315°C over 3 hours then maintained for 0.5 hours.

[0064] The reaction mixture was allowed to cool, milled and washed with acetone and water. The resulting polymer was dried in an air oven at 120°C. The polymer had a melt viscosity at 400°C, 1000sec<sup>-1</sup> of 0.28 kNsm<sup>-2</sup>.

[0065] By processes analogous to Examples 1a and 2a, further materials were prepared. A summary of the examples including mole ratios used in the preparations and Melt viscosities (MV) achieved are provided in Table A below, wherein the following abbreviations are used:

BDF                      4,4'-difluorobenzophenone

BP                    4,4'-dihydroxybiphenyl  
 DHB                4,4'-dihydroxybenzophenone  
 Bis-S    4,4'-dihydroxydiphenylsulphone

TABLE A

Polymer	Polymer Composition (mole ratio)				MV KNsm <sup>-2</sup>
	BDF	BP	DHB	Bis-S	
1a	1.02	0.33	0.134	0.536	0.34
1b	1.02	0.33	0.134	0.536	0.61
2a	1.02	0.33	-	0.67	0.28
2b	1.02	0.33	-	0.67	0.40

### Example 3 – Sulfonation of polymers

[0066] The polymers of Examples 1 and 2 were sulfonated by stirring each polymer in 98% sulfuric acid (3.84g polymer/100g sulfuric acid) for 21 hours at 50°C. Thereafter, the reaction solution was allowed to drip into stirred deionized water. Sulfonated polymer precipitated as free-flowing beads. Recovery was by filtration, followed by washing with deionized water until the pH was neutral and subsequent drying. In general, titration confirmed that 100 mole% of the biphenyl units had sulfonated, giving one sulfonic acid group, ortho to the ether linkage, on each of the two aromatic rings comprising the biphenyl unit.

### Example 4 – Membrane fabrication using NMP

[0067] Membranes were produced from the polymers of Examples 1 and 2 after sulfonation as described in Example 3 by dissolution of the sulfonated polymers in NMP (N-methylpyrrolidone) to form homogenous solutions, casting the solutions onto clear glass plates followed by drawing down, using a Gardner knife, to give 400 micron films. The NMP was then evaporated.

### Example 5 – Boiling Water Uptake

[0068] The following general procedure was followed to determine the Boiling Water Uptake of the membranes prepared.

[0069] 5cm x 5cm samples of membranes were selected. The thickness of the samples was related to the concentration of polymers in the solvent systems used to cast the membranes. The membranes were separately immersed in boiling deionized water (500ml)

for 60 mins, removed and dried quickly with lint-free paper to remove surface water, weighed, dried in an oven at 50°C for 1 day, allowed to cool to ambient temperature in a desiccator then weighed quickly. The % water-uptake was calculated as described below:

$$\% \text{ Water-uptake} = \frac{\text{Wet Weight} - \text{Dry Weight}}{\text{Dry Weight}} \times 100$$

#### Dry Weight

[0070] Table B below provides results for the polymers of Examples 1 and 2 when fabricated as described in Example 4. EW refers to the “equivalent weight”.

TABLE B

Sulfonated Polymer from	EW Theoretical	EW Actual	Boiling Water Uptake (%)
1a	683	677	143
1b	683	683	128
2a	690	694	140
2b	690	699	144

#### Example 6 – Membrane fabrication using water-based solvent formulations

[0071] Membranes were produced as described in Example 4, except that the sulfonated polymers were dissolved in a 50:50 mixture of acetone/water including 5 wt% NMP, at a sulfonated polymer concentration of 10 wt%. Dissolution may be undertaken at any temperature between ambient temperature and the boiling point of the solvent mixture. The falling ball viscosity of the above solutions was measured at 23°C using a Gilmont (Trade Mark) Instruments Falling Ball Viscometer using a stainless steel ball. Results for each solution, together with values for the boiling water uptake, measured as described in Example 5, are provided in Table C below.

TABLE C

Sulfonated Polymer from	Falling Ball Viscosity (cP)	Boiling Water Uptake (%)
1a	892	106
1b	1227	102
2a	174	140
2b	417	147

#### Example 7 – Preparation of dispersions of sulfonated polymers in water and membrane fabrication



**Example 7(a)**

[0072] The sulfonated polymers were each dissolved in a 50:50 mixture of acetone and water and, subsequently, the acetone was removed using a rotary evaporator under reduced pressure (20mm Hg/40°C), leaving approximately 20 wt% sulfonated polymer in water. The formulation produced is probably not a true solution but is more likely a very fine dispersion of the sulfonated polymer in water. The dispersions had very low viscosities and membranes cast therefrom tended to be brittle. However, the formulations could be used to impregnate fibers or fabrics and this may be facilitated by their low viscosities. Table D details the viscosity "before evaporation" for the formulations.

**Example 7(b)**

[0073] The procedure of Example 7(a) was followed except that, after removal of the acetone, some of the water was removed by using a rotary evaporator (20mm Hg/70°C) to produce more concentrated solutions (up to 50 wt% of sulfonated polymer in water). The formulation could be used to produce membranes. Table D details the viscosity of the formulations "after evaporation" of water, together with the "final concentration" of sulfonated polymer.

TABLE D

Sulfonated polymer from	Falling ball viscosity (cP)		Final conc. Of sulfonated polymer (% w/w)
	Before evaporation	After evaporation	
1a	82	282	36
1b	23	314	49
2a	18	480	54
2b	21	680	53

**Example 7(c)**

[0074] The procedure of Example 7(b) was followed, except that a coalescing agent (NMP or ethylene glycol) was added as detailed in Table E to facilitate preparation of membranes. Membranes were prepared and boiling water uptakes (%) determined as described above. Results are provided in Table E below.

TABLE E

Sulfonated Polymer from	EW Theoretical	EW Actual	Amount NMP (wt%)	Final conc. of sulfonated polymer (%w/w)	Boiling Water Uptake (%)
1a	683	691	10	32	106
1b	683	701	15	42	102
2a	690	710	15	46	135
2b	690	709	15	45	158

[0075] It should be appreciated from Table E that no increase in EW is observed, suggesting the procedure described does not cause a loss of sulfonic acid groups.

#### Example 8 – Membrane fabrication using water-based solvent formulations

[0076] Membranes were produced as described in Example 4, except that the sulfonated polymers were dissolved in a 50:50 mixture of THF/water including 5 wt% NMP, at a sulfonated polymer concentration of 10 wt%. The values for the boiling water uptake measured as described in Example 5, are provided in Table F below. The falling ball viscosity of the above solutions were measured at 23°C using a Gilmont® Instruments Falling Ball Viscometer using a stainless steel ball.

TABLE F

Sulfonated Polymer from	Falling Ball Viscosity (cP)	Boiling Water Uptake (%)
1a	1034	109
2a	4964	136

#### Example 9 – Preparation of dispersions of sulfonated polymers in water and membrane fabrication

##### Example 9(a)

[0077] The sulfonated polymers were each dissolved in a 50:50 mixture of THF and water and, subsequently, the THF was removed using a rotary evaporator under reduced pressure (20mm Hg/40°C), leaving approximately 17 wt% sulfonated polymer in water. The formulation produced is probably not a true solution but is more likely a very fine dispersion of the sulfonated polymer in water. The dispersion had very low viscosity and membranes cast therefrom tended to be brittle. The aqueous solutions/dispersions could be used to

impregnate fibers of fabrics. Table G details the viscosity "before evaporation" for the formulations.

**Example 9 (b)**

[0078] The procedure of Example 9(a) was followed except that, after removal of the THF, some of the water was removed by using a rotary evaporator (20mm Hg/70°C) to produce more concentrated solutions. The formulation could be used to produce membranes. Table G details the viscosity of the formulations "after evaporation" of water, together with the concentration of sulfonated polymer.

TABLE G

Sulfonated polymer from	Falling ball viscosity (cP)		Sulfonated polymer conc. (% w/w)
	Before evaporation	After evaporation	
1a	50	104	22
2a	800	1068	21

**Example 9(c)**

[0079] The procedure of Example 9(b) was followed, except that a coalescing agent (NMP or ethylene glycol) was added to facilitate preparation of membranes. Membranes were prepared and boiling water uptakes (%) determined as described above. Results are provided in Table H below.

Table H

Sulfonated Polymer from	Boiling Water Uptake (%)	Final Sulfonated Polymer conc. (% w/w)
1b	98	20.9
2a	123	20

[0080] Attention is directed to all papers and documents which are filed concurrently with or previous to this specification in connection with this application and which are open to public inspection with this specification, and the contents of all such papers and documents are incorporated herein by reference.

[0081] All of the features disclosed in this specification (including any accompanying claims, abstract and drawings), and/or all of the steps of any method or process so disclosed, may be combined in any combination, except combinations where at least some of such features and/or steps are mutually exclusive.

**[0082]** Each feature disclosed in this specification (including any accompanying claims, abstract and drawings) may be replaced by alternative features serving the same, equivalent or similar purpose, unless expressly stated otherwise. Thus, unless expressly stated otherwise, each feature disclosed is one example only of a generic series of equivalent or similar features.

**[0083]** The invention is not restricted to the details of the foregoing embodiment(s). The invention extends to any novel one, or any novel combination, of the features disclosed in this specification (including any accompanying claims, abstract and drawings), or to any novel one, or any novel combination, of the steps of any method or process so disclosed.

**[0084]** The exemplary embodiment has been described with reference to the preferred embodiments. Obviously, modifications and alterations will occur to others upon reading and understanding the preceding detailed description. It is intended that the exemplary embodiment be construed as including all such modifications and alterations insofar as they come within the scope of the appended claims or the equivalents thereof.